



Synthesis of poly(aminopropyl/methyl)silsesquioxane particles as effective Cu(II) and Pb(II) adsorbents

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ABSTRACT

Poly(aminopropyl/methyl)silsesquioxane (PAMSQ) particles have been synthesized by a one-step hydrolytic co-condensation process using 3-aminopropyltriethoxysilane (APTES) and methyltrimethoxysilane (MTMS) as precursors in the presence of base catalyst in aqueous medium. The amino functionalities of the particles could be controlled by adjusting the organosilanes feed ratio. The compositions of the amino-functionalized polysilsesquioxanes were confirmed by FT-IR spectroscopy, solid-state ^{29}Si NMR spectroscopy, and elemental analysis. The strong adsorbability of Cu(II) and Pb(II) ions onto PAMSQ particles was systematically examined. The effect of adsorption time, initial metal ions concentration and pH of solutions was studied to optimize the metal ions adsorbability of PAMSQ particles. The kinetic studies indicated that the adsorption process well fits the pseudo-second-order kinetics. Adsorption phenomena appeared to follow Langmuir isotherm. The PAMSQ particles demonstrate the highest Cu(II) and Pb(II) adsorption capacity of 2.29 mmol/g and 1.31 mmol/g at an initial metal ions concentration of 20 mM, respectively. The PAMSQ particles demonstrate a promising application in the removal of Cu(II) and Pb(II) ions from aqueous solutions.

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1. Introduction

The pollution of heavy-metal ions has already become a worldwide serious problem that endangers the environment and health of human beings [1,2]. There are a variety of methods that can be used for removing of heavy-metal ions including liquid–liquid extraction, chemical precipitation, metal replacement, ion exchange [3,4], electrolysis [5], and membrane separation [6]. Adsorption using suitable adsorbents has also been widely used for the concentration and retrieval of metal ions. A variety of new adsorbents are currently being explored, including activated carbon [7], chelating resins [8], biosorbents [9], and mesoporous silica [10]. And nowadays, seeking for novel adsorbents for heavy-metal ions with high efficiency and low cost has become the main direction of the research on the adsorption and removal of heavy-metal ions.

Modified matrices with amino groups have attracted a great attention for metal uptake. Pearson's hard–soft, acid–base (HSAB) principle states that hard (Lewis) acids prefer to bind to hard (Lewis) bases and soft (Lewis) acids prefer to bind to soft (Lewis) bases [11]. The RNH_2 are considered to be hard Lewis base

according to Pearson's HSAB principle and selecting RNH_2 as functional groups should create an adsorbent that displays affinity for adsorption of hard Lewis acid, such as copper. Lam and co-workers [12] demonstrated that Cu(II) was selectively removed by NH_2 -MCM-41 containing NH_2 adsorption sites from binary $\text{AgNO}_3/\text{Cu}(\text{NO}_3)_2$ solutions. Yantasee et al. [13] found amine-functionalized activated carbon had an affinity for metal ions in decreasing order of $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+}$ and with a saturation loading capacity of 0.86 mmol of Cu/g. I.M. El-Nahhal and co-workers have prepared a series of amino group functionalized polysiloxane-immobilized ligand systems via the sol–gel process and found their application in separation of heavy metal ions from aqueous solution [14–18].

In recent years, there has been intense interest in the preparation and application of functional polysilsesquioxane particles [19–21]. We have reported the strong adsorbability of Ag(I) ions onto poly(3-mercaptopropylsilsesquioxane) (PMPSQ) microspheres recently [22]. Beari et al. [23] have studied the hydrolytic condensation of 3-aminopropyltriethoxysilane (APTES) in aqueous solutions and found the hydrolysis and condensation products of APTES was not precipitated from the solution even after several weeks due to their excellent water solubility.

In this paper, we report a one-step synthetic process for synthesizing amino-functionalized polysilsesquioxane having high content of amino groups to develop an efficient adsorbent of

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Nomenclature

APTES	3-aminopropyltriethoxysilane
b	Langmuir constant (L/mmol)
C_0	initial metal ions concentration (mmol/L)
C_e	equilibrium metal ions concentration (mmol/L)
h	initial adsorption rate ($\text{mmol g}^{-1} \text{min}^{-1}$)
k_1	pseudo-first-order rate constant (min^{-1})
k_2	pseudo-second-order rate constant ($\text{g mmol}^{-1} \text{min}^{-1}$)
m	mass of the adsorbent (g)
MTMS	methyltrimethoxysilane
PAMSQ	poly(aminopropyl/methyl)silsesquioxane
PMSQ	poly(methylsilsesquioxane)
q_e	adsorption capacity (mmol/g)
q_m	theoretical saturation adsorption capacity (mmol/g)
q_t	adsorption capacity at t (mmol/g)
R^2	regression coefficient
t	time (min)
V	the solution volume (L)

heavy metals. Poly(aminopropyl/methyl)silsesquioxane (PAMSQ) particles were obtained by hydrolytic co-condensation of 3-aminopropyltriethoxysilane (APTES) with methyltrimethoxysilane (MTMS) in aqueous medium. The PAMSQ particles have the ability to effectively remove the Cu(II) and Pb(II) ions from the aqueous solution. The effect of adsorption time, initial metal ions concentration, and solution pH was studied by a static adsorption method to optimize the Cu(II) and Pb(II) adsorbability of PAMSQ particles.

2. Experimental

2.1. Materials

3-Aminopropyltriethoxysilane (APTES, $\geq 98.0\%$) was purchased from Diamond Advanced Material of Chemical Inc. Methyltrimethoxysilane (MTMS, $\geq 98.0\%$) was purchased from Jiangsu Danyang Organosilicon Material Industrial Corporation. Ammonium hydroxide solution (NH_4OH , 25%), copper sulfate pentahydrate and lead nitrate of analytical reagent grade were commercially obtained and used as received.

2.2. Synthesis of PAMSQ particles by hydrolytic co-condensation process

PAMSQ particles were prepared using base catalyzed sol-gel process in aqueous medium. The mixture of APTES and MTMS at different molar ratios was added to 100 mL of water, maintaining 10% weight percentage. Ammonium hydroxide solution (0.16 mL) was added into the above solution. The reaction was continued overnight at room temperature. Then the resulting precipitate was filtrated with millipore filter membrane ($0.22 \mu\text{m}$) and rinsed thoroughly with distilled water and ethanol several times to remove the residual NH_4OH as well as unreacted monomers or oligomers. Finally, the products were dried in vacuum and the PAMSQ particles were attained.

2.3. Adsorption of Cu(II) and Pb(II) onto the PAMSQ particles

Batch adsorption experiments were conducted using PAMSQ particles as a adsorbent to adsorb Cu(II) or Pb(II) ions from aqueous single metal ion solutions. The sample pH was adjusted to the desired value with HNO_3 or ammonia solution. The batch adsorption experiments were conducted in a shaker bath kept at

constant temperature of 20°C at 100 rpm. After a desired period of adsorption, the particles were filtered from the solution with millipore filter membrane ($0.22 \mu\text{m}$). The final concentrations of the metal ions in the solution were analyzed by inductively coupled plasma, atomic emission spectrometry (ICP-AES, IRIS 1000, Thermo Elemental). The equilibrium adsorption capacity was calculated from Eq. (1).

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where q_e (mmol/g) is the adsorption capacity and C_0 (mmol/L) and C_e (mmol/L) are respectively the initial and equilibrium metal concentrations. V (L) is the solution volume, and m (g) is the weight of the adsorbent.

2.4. Measurements

Elemental analyses were performed with a Vario EL III elemental analyzer (Elementar Analysen systeme GmbH, Germany). FT-IR spectra were recorded on a iS10 FT-IR spectrophotometer (Nicolet, USA). The samples were mixed with potassium bromide and pressed to a disk to measure the absorption spectrum. High-resolution solid-state ^{29}Si NMR spectra were measured at room temperature on a Bruker Avance 400 MHz spectrometer (silicon frequency 99.36 MHz) equipped with a Bruker solid-state accessory. Spectra were obtained using a broadband probehead with a 4 mm double air bearing magic-angle spinning assembly. Chemical shifts of silicon atoms in silsesquioxane compounds are referred to using the traditional terminology T^n , where the superscript corresponds to the number of oxygen bridges to other silicon atoms. Thus, an uncondensed monomer was designated T^0 and a fully condensed polymer with no residual silanols was assigned as T^3 silicon atoms [24].

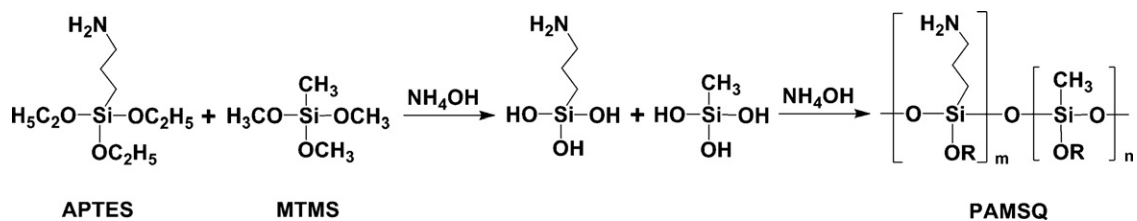
A field emission SEM (JSM-7401F FE-SEM, JEOL Ltd., Japan) was utilized to study the morphology of the PAMSQ particles. The particles were sputter-coated with gold for SEM observations. Specific surface area data were performed on a Micromeritics ASAP 2020 surface area and porosity analyzer with BET method. TGA was performed on a SDT Q600 (TA Instruments, USA) thermal analyzer at a heating rate of $10^\circ\text{C min}^{-1}$ in air.

3. Results and discussion

3.1. Synthesis and properties of PAMSQ particles

Synthesis of PAMSQ particles with controllable amount of aminopropyl functional groups using APTES and MTMS as precursors by hydrolytic co-condensation process were conducted (Scheme 1). Generally, hydrolytic condensation of the organotrimethoxysilanes in water or ethanol-water was quite rapid under basic conditions [23–25]. Initial hydrolysis of the APTES and MTMS resulted in silanol oligomers. Silanol (Si-OH) was very reactive and then condensed to form polysilsesquioxanes in the presence of base catalyst. The amino groups of APTES could increase the pH of solution and accelerates the hydrolytic co-condensation process. Simultaneous hydrolysis of APTES and MTMS led to co-condensation, but the product state was different with the variation of APTES/MTMS molar ratios. If the APTES molar ratio in the precursors was less than 40%, white precipitate appeared. However, the co-condensation products were not precipitated from the solution when the APTES molar ratio in the precursors was above 50% due to the excellent solubility of co-condensed PAMSQ in water.

SEM images show morphology of polysilsesquioxanes particles (see Fig. 1). The PMSQ particles prepared from MTMS alone are spherical with a medium size of $2.0 \mu\text{m}$. The particle aggregation was quite evident for the copolymerized PAMSQ particles



Scheme 1. Schematic illustration of the synthetic strategy for PAMSQ particles. Note that "OR" can present either silanol (OH) or other silane units

and the particle size decreased with increasing APTES amount in the APTES/MTMS mixtures, as seen in Fig. 1b–d. The results could be due to the excellent solubility of APTES in water, which makes the copolymerized PAMSQ particles to be more hydrophilic. Additionally, the amino groups of APTES raised pH of reaction solution and catalyze the hydrolytic co-condensation reactions of APTES and MTMS. Increase in hydrolysis rates with increasing pH led to a higher nucleation rate, which also resulted in a larger number of particles but a smaller final particle size [24].

Table 1 shows the properties of polysilsesquioxanes particles. Amino group contents of PAMSQ particles determined by element analysis were lower than the theoretical values. The results could be due to the excellent solubility of APTES and its hydrolysis and condensation products in water [23]. These results are consistent with those reported by Liu et al. [20] that copolymerized aminopropyl/phenylsilsesquioxane microparticles synthesized from the hydrolytic co-condensation of APTES and phenyltriethoxysilane (PTES). The specific surface areas of the polysilsesquioxanes particles were evaluated using the BET method as shown in Table 1.

The relatively small BET surface area values were due to complete condensation of polysilsesquioxanes.

The influence of amino groups content on Cu(II) and Pb(II) adsorption onto the PAMSQ particles was investigated. As shown in Table 1, the aminopropyl functionalized PAMSQ samples revealed a high affinity towards Cu(II) and Pb(II), and the adsorption capacity of metal ions onto the PAMSQ particles increase with increasing amino groups content. However, the unmodified PMSQ without amino groups adsorbed only small amount of Cu(II) and Pb(II) ions. The results of Table 1 suggest that the mechanism of adsorption involves primarily metal ion complexation by the amino groups. High amino group contents make PAMSQ3 fit as a representative copolymerized product to be used for further studies in adsorption experiment.

Solid-state ^{29}Si NMR spectra are powerful methods for characterizing the chemical structure of polysilsesquioxane frameworks. According to Arkhireeva et al. [26], in the case of the polysilsesquioxane derived from MTMS, resonances at -65.9 , -57.1 , -48.5 ppm can be assigned to T^3 , T^2 and T^1 species, respectively. And Caravajal et al. [27] reported the ^{29}Si NMR spectra

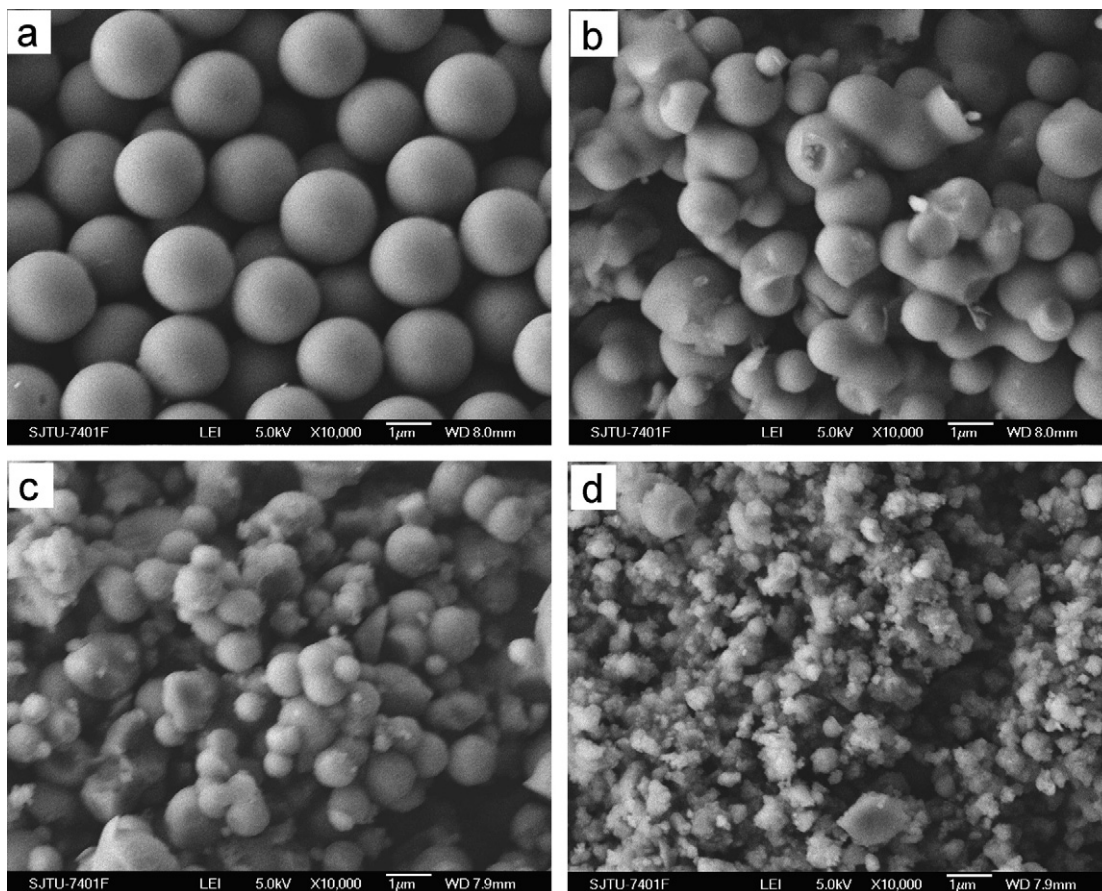


Fig. 1. SEM images of polysilsesquioxanes particles: (a) PAMSQ, (b) PAMSQ1, (c) PAMSQ2 and (d) PAMSQ3.

Table 1
Properties of polysilsesquioxanes particles.

Samples	APTES in comonomers (mol%)	^a Amino content in PAMSQ (mol%)	BET surface area (m ² /g)	^b Cu(II) adsorption capacity (mmol/g)	^b Pb(II) adsorption capacity (mmol/g)
PMSQ	0	0	4.3	0.13	0.17
PAMSQ1	20	15	4.8	0.80	0.58
PAMSQ2	30	22	6.7	1.62	0.90
PAMSQ3	40	27	5.0	2.25	1.14

^a The amino content in PAMSQ is determined by elemental analysis of nitrogen content.

^b Initial metal ions concentration: 10 mM, adsorption time: 5 h, adsorbent dose: 2 g/L.

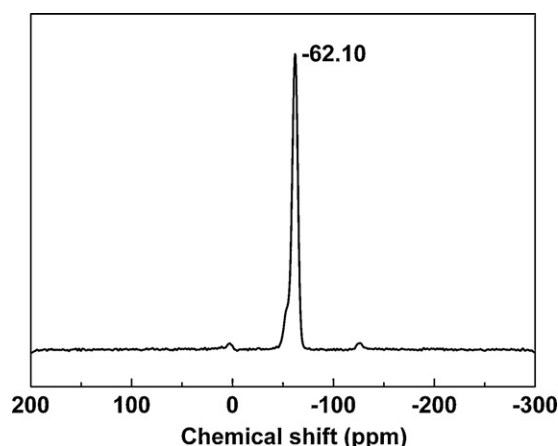


Fig. 2. Solid-state ²⁹Si NMR spectrum of PAMSQ3 particles.

exhibited major peaks in the regions of -66 , -58 and -49 ppm, due to the silicons of the attached $\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ moiety of APTES-modified silica. Fig. 2 shows solid-state ²⁹Si NMR spectrum of PAMSQ3 particles. There is one large peak at -62.1 ppm and a weak shoulder peak at about -53 ppm assigned to fully condensed T³ and linear T² species, respectively. The formation of T¹ and T⁰ species is insignificant, suggesting that the co-condensation is quite completed [28].

Fig. 3 shows IR spectra of PMSQ and PAMSQ3 particles. PMSQ and PAMSQ3 exhibit well-defined methyl group and Si–O–Si absorption bands at: 2970 , ca. 2921 – 2934 cm^{-1} ($\nu_{\text{C-H}}$), 1410 cm^{-1} ($\delta_{\text{C-H}}$ in Si–R), 1272 cm^{-1} ($\delta_{\text{C-H}}$ in Si–R), ca. 1119 – 1127 , ca. 1032 – 1036 cm^{-1} ($\nu_{\text{Si-O-Si}}$), and 778 cm^{-1} ($\nu_{\text{Si-C}}$) [29,30]. Si–O–Si stretching peaks at 1119 – 1127 cm^{-1} indicate the presence of cage-structure while adsorption at 1032 – 1036 cm^{-1} show that the ordered structure is probable ladderlike or layered [20,30]. The spectrum of PAMSQ3 showed bands due to aminopropyl groups at

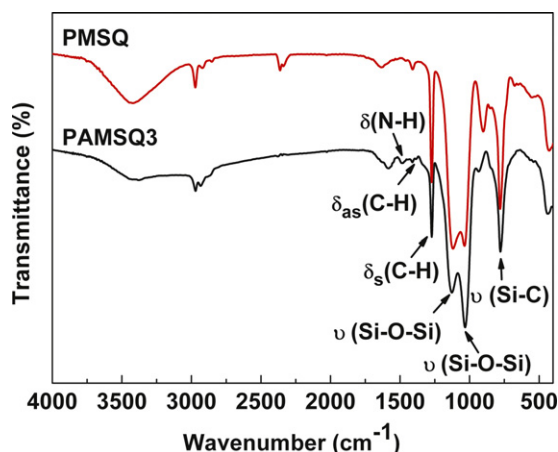


Fig. 3. IR spectra of PMSQ and PAMSQ3 particles.

1482 cm^{-1} ($\delta_{\text{N-H}}$), 3376 cm^{-1} ($\nu_{\text{N-H}}$), 2934 and 2970 cm^{-1} ($\nu_{\text{C-H}}$). A broad band around 3400 cm^{-1} could be attributed both to the adsorbed water and to the Si–OH group [29].

The thermal stability of the PMSQ and PAMSQ3 in air was investigated using TGA (Fig. 4). Weight loss in the 100 – 250 °C range for polysilsesquioxane is probably due to the residual reaction of alkoxypropyl groups [26]. The thermal reduction of polysilsesquioxane in the 250 – 700 °C range appeared to be mainly due to the decomposition of organic moiety groups [24]. The thermal decomposition temperatures of the PAMSQ3 particles in air, at 5% weight loss and at 10% weight loss are 257 °C and 370 °C, respectively. The TGA result shows that both the PMSQ and PAMSQ3 particles have good thermal stability.

3.2. Adsorption kinetics of Cu(II) and Pb(II) onto the PAMSQ3 particles

The kinetics of adsorption is one of the important characteristics that define the efficiency of adsorption. The effect of contact time on the adsorption of Cu(II) and Pb(II) onto the PAMSQ3 particles is shown in Fig. 5. The kinetic curve showed that the adsorption was rapid for the first 10 min, when the adsorption capacity reaches up to 1.49 mmol/g and 0.58 mmol/g for Cu(II) and Pb(II), respectively, and then slowed gradually. The initial rapid step of metal ions adsorption may be attributed to the physical and reactive adsorption between metal ions and the amino groups on the surface of the PAMSQ3 particles. However, the subsequent slow step is attributable to the adsorption inside the particles, representing the diffusion of Cu(II) and Pb(II) ions into the inner of the particles over a long period. Experimental results suggest that the amount of metal ions adsorbed increased with increasing adsorption time and reached equilibrium at 300 min for Cu(II) and Pb(II). Hence, in the present study, we used 300 min contact time for further experiments.

Pseudo-first-order and pseudo-second-order models [31] were used to test the experimental data and thus elucidate the

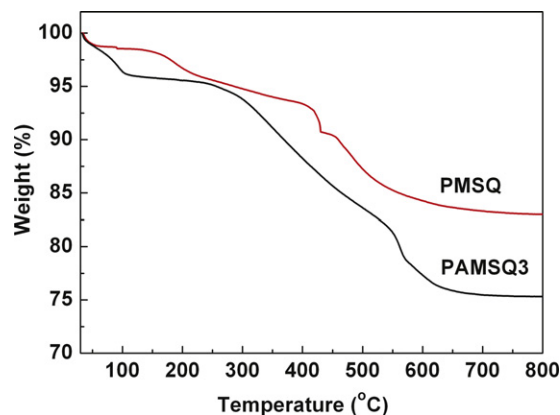


Fig. 4. TGA curves of PMSQ and PAMSQ3 in air.

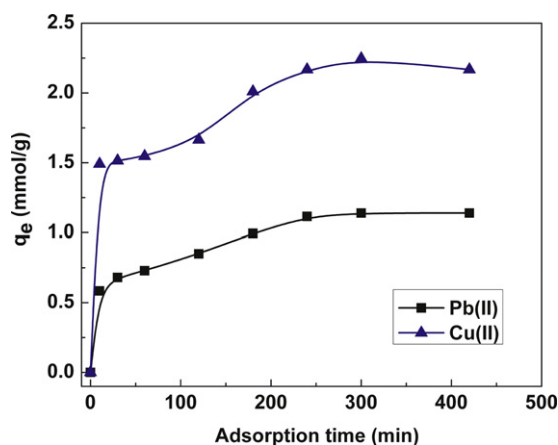


Fig. 5. Effect of adsorption time on Cu(II) and Pb(II) adsorption onto PAMSQ3 particles (initial metal ions concentration: 10 mM; adsorbent dose: 2 g/L).

adsorption kinetic process. The Lagergren pseudo-first-order kinetic model, represented as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

where q_e and q_t are the amounts of metal ions adsorbed (mmol/g) at equilibrium and time t , respectively, and k_1 (min^{-1}) is the pseudo-first-order rate constant. The q_e and rate constant k_1 were calculated by plotting the $\log(q_e - q_t)$ vs. t . As seen from Fig. 6, the pseudo-first-order model does not fit the data well. The experimental and calculated q_e values, pseudo-first-order rate constants and regression coefficient (R^2) values are presented in Table 2. The calculated q_e values in the pseudo-first-order model were not in agreement with the experimental q_e values, suggesting that the adsorption of Cu(II) and Pb(II) does not follow pseudo-first-order kinetics. In order to find a more reliable description of the adsorption kinetics of Cu(II) and Pb(II) ions onto the particles, a pseudo-second-order kinetic model was applied to the experimental data.

The pseudo-second-order equation can be written as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

where q_e and q_t are defined as in the pseudo-first-order kinetic model; k_2 is the pseudo-second-order rate constant. The slope and intercept of the linear plot t/q_t vs. t in Fig. 7 yielded the values

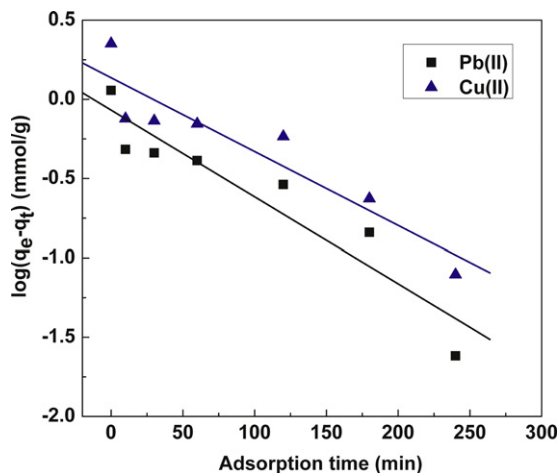


Fig. 6. Pseudo-first-order kinetic plots for the adsorption of Cu(II) and Pb(II) onto PAMSQ3 particles.

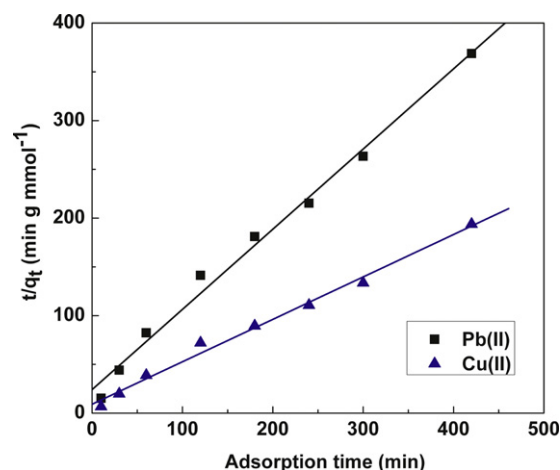


Fig. 7. Pseudo-second-order kinetic plots for the adsorption of Cu(II) and Pb(II) onto PAMSQ3 particles.

of q_e and k_2 . Additionally, the initial adsorption rate (h) can be determined from k_2 and q_e values using $h = k_2 q_e^2$. The regression coefficients (R^2) and several parameters obtained from the pseudo-second-order kinetic model are also shown in Table 2. As seen from Table 2, the calculated q_e values are in good agreement with experimental q_e values. Moreover, the obtained R^2 values for Cu(II) and Pb(II) adsorption both are above 0.99. Hence, the adsorption kinetics could well be approximated more favorably by pseudo-second-order kinetic model for Cu(II) and Pb(II) onto the PAMSQ3 particles. The pseudo-second-order model was developed based on the assumption that the determining rate step may be chemisorption promoted by covalent forces through the electron exchange, or valency forces through electrons sharing between adsorbent and adsorbate [31], indicating that the adsorption of Cu(II) and Pb(II) on PAMSQ3 particles is mainly the chemically reactive adsorption.

3.3. Effect of initial metal ions concentration and adsorption isotherm

The effect of the initial metal ions concentration on adsorption of Cu(II) and Pb(II) onto the PAMSQ3 particles is shown in Fig. 8. At a lower initial metal ions concentration, abundant aminopropyl groups on the surface of the PAMSQ particles can react with metal ions, resulting in a significantly increased adsorption of Cu(II) and Pb(II). Then the adsorption process gradually becomes slow with increasing initial metal ions concentration.

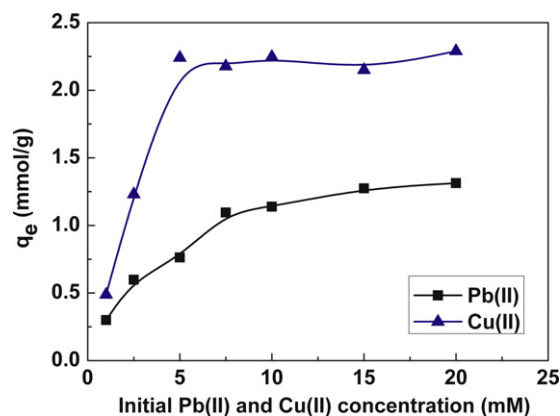


Fig. 8. Effect of initial metal ions concentration on adsorption of Cu(II) and Pb(II) on PAMSQ3 particles (initial metal ions concentration: 1–20 mM; adsorption time: 5 h; adsorbent dose: 2 g/L).

Table 2
Kinetic model equations for Cu(II) and Pb(II) adsorption onto the PAMSQ3 particles.

Metal ions	q_e (exp.) (mmol/g)	Pseudo-first-order			Pseudo-second-order			
		k_1 (min ⁻¹)	q_e (cal.) (mmol/g)	R^2	k_2 (g mmol ⁻¹ min ⁻¹)	h (mmol g ⁻¹ min ⁻¹)	q_e (cal.) (mmol/g)	R^2
Cu(II)	2.25	0.01073	1.37	0.8695	0.021	0.11	2.30	0.9915
Pb(II)	1.14	0.01262	0.85	0.8830	0.028	0.04	1.22	0.9908

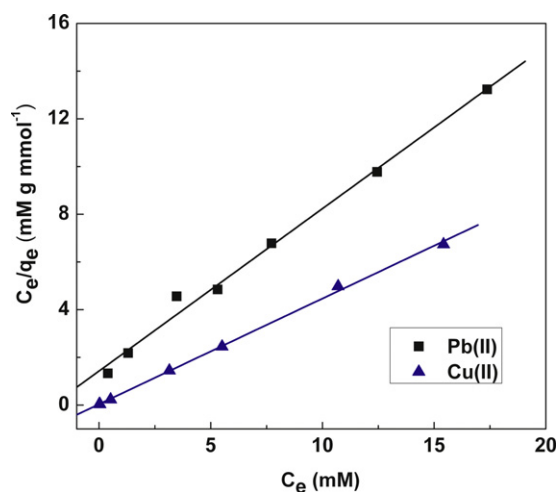


Fig. 9. Langmuir plots for Cu(II) and Pb(II) adsorption on the PAMSQ3 particles (initial metal ions concentration: 1–20 mM; adsorption time: 5 h; adsorbent dose: 2 g/L).

Fig. 9 shows the adsorption isotherms of Cu(II) and Pb(II) by the PAMSQ3 particles at 20 °C. The adsorption data were plotted according to Langmuir equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (4)$$

where q_m and b are the characteristic Langmuir parameters. q_m is the theoretical saturation adsorption capacity of the monolayer (mmol/g) and b is a constant related to the intensity of adsorption. Plotting C_e/q_e against C_e gives straight lines as shown in Fig. 9. Table 3 displays the coefficients of the Langmuir model along with regression coefficients (R^2). As seen from Table 3, the R^2 values for the Langmuir isotherm models were both above 0.99, suggesting that the Langmuir model closely fits the experimental results. The calculated q_m values are in good agreement with those experimentally found. PAMSQ3 particles possess a strong capability to adsorb Cu(II) and Pb(II) ions from aqueous solutions, indicating a great potential as a high efficiency adsorbent.

The variations of metal ions uptake on various adsorbents are associated with adsorbent properties such as structure, functional groups, and specific surface area. Table 4 shows the comparison of the maximum adsorption capacity of PAMSQ for Cu(II) and Pb(II) onto various adsorbents reported in the literature. The results demonstrate that the adsorption capacities of PAMSQ3 particles for Cu(II) and Pb(II) were high when compared to several other adsorbents. Therefore, it could be believed that the PAMSQ3 particles synthesized from common silane coupling agent through a

Table 3
Coefficients of Langmuir isotherms.

Metal ions	q_m (exp.) (mmol/g)	q_m (cal.) (mmol/g)	b (L/mmol)	R^2
Cu(II)	2.29	2.26	11.82	0.9986
Pb(II)	1.31	1.47	0.48	0.9925

facile method under moderate condition would have a promising application as a cost-effective adsorbent.

3.4. Effect of solution pH on adsorption

Fig. 10 shows the effect of the solution pH on the adsorptions of Cu(II) and Pb(II) by PAMSQ3 particles, respectively. The pH in a range of 2.0–5.0 was chosen to avoid the precipitations of Cu(OH)₂ and Pb(OH)₂. The adsorption capacities increased with an increase in solution pH in the pH range of 2.0–5.0 and no adsorption was observed at pH 2.0. This could be attributable to a competitive adsorption between metal ions and H⁺ ions on PAMSQ3 particles. At low pH value, the adsorption of metal ions is decreased because high concentrations of competitive H⁺ ions occupy the adsorption sites, whereas the protonated amino groups are deprotonated with increasing pH value, enhancing metal ions adsorbability [15,44]. Therefore, the solution pH around 5.0 could be optimal for the application of the PAMSQ3 particles as efficient Cu(II) and Pb(II) adsorbent.

3.5. Adsorption mechanism of metal ions onto PAMSQ particles

Sorption is broadly defined as the transferring of ions from the solution phase to the solid phase via various mechanisms such as physical and chemical adsorption, surface precipitation, or solid-state diffusion or fixation [45]. According to hard and soft acids and bases theory of Pearson [11], aminopropyl group functionalized PAMSQ has bonding ability with heavy metal ions such as Cu(II) and Pb(II). The FTIR spectra of PAMSQ3 particles before and after adsorption of Cu(II) ion are shown in Fig. 11. Appearance of a sharp peak at 619 cm⁻¹ after adsorption of Cu(II) on PAMSQ3 is assigned to the stretching vibration of N–Cu bond formed during complexation process [37]. The FTIR results confirm that nitrogen of PAMSQ3 particles are actively participated during the adsorption process through complexation with Cu(II) ion. So the adsorption mechanism of metal ions onto PAMSQ3 particles involves primarily metal ions complexation by the amino groups.

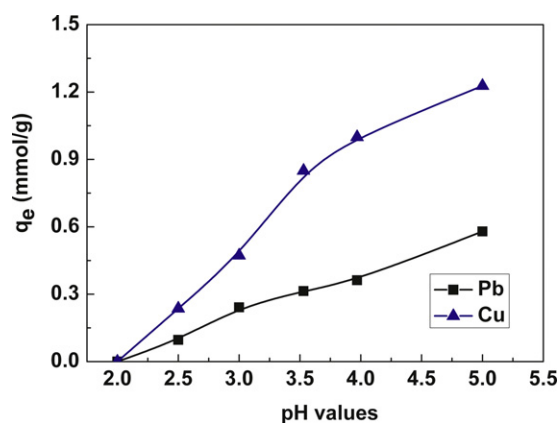
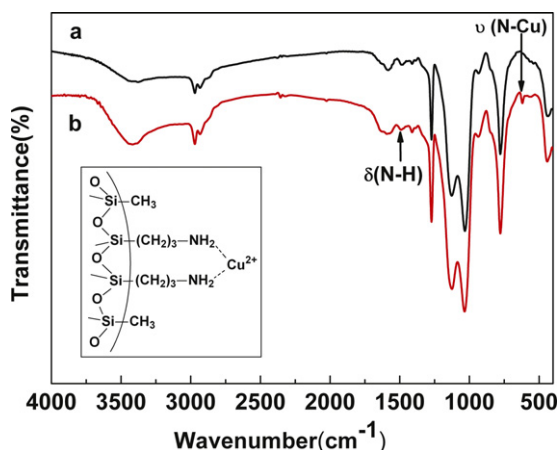


Fig. 10. Effect of the pH on adsorption of Cu(II) and Pb(II) on PAMSQ3 particles (initial metal ions concentration: 2.5 mM; adsorption time: 5 h; adsorbent dose: 2 g/L).

Table 4

Comparison of maximum adsorption capacity of PAMSQ for Cu(II) and Pb(II) onto various adsorbents reported in the literature.

Adsorbents	Adsorption capacity (mg/g)		Ref.
	Cu(II)	Pb(II)	
SBA-15 mesoporous silica with melamine-based dendrimer amines	126	130	[32]
Silica gel chemically modified by triethylenetetraminomethylenephosphonic acid	19.8	16.8	[33]
Silica gel modified with 5-amino-1,3,4-thiadiazole-2-thiol	1.21	1.54	[34]
Ethylenediaminetriacetic acid functionalized silica-gel	99.4		[35]
4-Amine-2-mercaptopyrimidine modified silica gel		80.19	[36]
2-Aminophenylaminopropylpolysiloxane	130.91		[16]
Epichlorohydrin cross-linked xanthate chitosan	43.47		[37]
Aminated polyacrylonitrile nanofibers	116.52		[38]
Porous chitosan monoliths	141.8		[39]
PS-EDTA resin	42.1	32.1	[40]
2-((2-Aminoethylamino)methyl)phenol-functionalized activated carbon	12.1	16.2	[41]
Iron oxide coated sewage sludge	17.3	42.4	[42]
<i>Ulva lactuca</i> algae	112	230	[9]
Potassium hydroxide treated pine cone powder	19.22	26.27	[43]
PAMSQ particles	146	272	This work

**Fig. 11.** FTIR spectra of PAMSQ3 particles (a) before adsorption and (b) after adsorption of Cu(II). Inset: scheme of copper ions binding.

4. Conclusions

Amino-functionalized polysilsesquioxane particles have been synthesized by hydrolytic co-condensation using APTES and MTMS as precursors in the presence of base catalyst in aqueous medium. The process is a one-step co-condensation synthetic route where the functionalities of the particles can be easily controlled by changing the organosilanes feed ratio. The results of solid-state NMR spectroscopy, FT-IR analysis, and elemental analysis confirmed the co-condensation between organosilanes. The PAMSQ particles had shown as an efficient adsorbent for the removal of Cu(II) and Pb(II). The adsorption behavior of Cu(II) and Pb(II) onto PAMSQ particles is influenced by the adsorption time, initial concentration of metal ions, and solution pH. The kinetic studies indicated that the adsorption process well fits the pseudo-second-order kinetics with a rapid initial adsorption rate. The experimental data was well fit by the Langmuir isotherm model. The PAMSQ particles demonstrate the highest Cu(II) and Pb(II) adsorption capacity of 2.29 mmol/g and 1.31 mmol/g at an initial metal ions concentration of 20 mM, respectively. Therefore, there are good prospects for the PAMSQ particles in practical applications for the removal of Cu(II) and Pb(II) ions from their aqueous solutions.

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